

**MOLECULAR-STATISTICAL DESCRIPTION
OF NONUNIFORMLY DEFORMED SPECIMENS.
3. CALCULATION OF THE DIAGRAM OF EXTENSION
AND COMPRESSION OF A ONE-DIMENSIONAL STATISTICAL
MODEL OF DEFORMATION OF A MOLECULAR CRYSTAL**

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A system of nonlinear equations whose solution determines the dependence of the equilibrium concentration of vacancies on the molecular length of a chain with occupied and unoccupied sites has been obtained using the variational method. Numerical solution of this system made it possible to calculate the free energy, the thermodynamic Gibbs potential, and the deforming force as functions of the macroscopic deformation of the linear chain. As a result, a theoretical diagram of extension and compression for a one-dimensional model has been constructed.

In recent times, it has become possible to construct a statistical theory of deformed molecular crystal lattices with defects [1, 2], to which one cannot, in principle, apply the traditional methods of elasticity theory in studying a microstructure, since the foundation of this theory is formed by the notion of a continuous, i.e., model, medium. Therefore, the use of these methods is confined to the region of small deformations beyond which we have an unsolved problem of description of the nonlinear deformation of real bodies (with defects) with allowance for their plasticity and the actual absence of the continuity of a material. For practical implementation of the possibilities of the developed two-level molecular-statistical description of crystal specimens with vacancies it is desirable to have an exactly solvable statistical model whose properties can be investigated by analytical methods. Since the state of a deformed crystal with vacancies is described in the general case by a fairly complex nonlinear integral equation with field parameters (the field of microscopic deformation tensor and the concentration field of unoccupied lattice sites), for solution of the problem posed we confine ourselves here, just as previously [2, 3], to consideration of uniformly deformed linear specimens subjected to uniaxial extension and compression.

Description of the One-Dimensional Statistical Model of a Deformed Specimen and Obtaining the Variational Equation. Earlier [1–3], within the framework of the two-level molecular-statistical approach [4] whose foundation is formed by the method of conditional distributions [5], the method of Bogolyubov, Born, Green, Kirkwood, and Yvon (BBGKY), and the method of thermodynamic functionals [6], we developed a statistical model of uniaxial deformation of a molecular crystal with thermal vacancies. It represents a molecular chain of length L consisting of M sites at which N molecules are statistically distributed, and their interaction is described by the Lennard-Jones potential. Expressions [3] were obtained for the lowest distribution functions of particles (molecules) and the free energy as a function of the concentration $n = N/M$ and the uniform microdeformation λ of each link of the chain of length $R = L/M$, which are the internal parameters of the model. To determine the equilibrium values of the parameters n and λ we use the extremum principle of thermodynamic potentials of a system of many particles. Taking into account the retained number N of molecules in a deformed chain, we vary the free energy by n and λ for a fixed value of the molecular length

$$l = \frac{L}{N} = \frac{LM}{NM} = \frac{R}{n} = \frac{R_0(1+\lambda)}{n}, \quad \lambda = \frac{(R-R_0)}{R_0}, \quad (1)$$

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i.e., for a certain value of the length L of the chain. Here R_0 is the length of the undeformed link playing the role of a microcell for a one-dimensional chain and l is the one-dimensional analog of molecular volume in three-dimensional specimens. Expression (1) is the coupling equation for the internal parameters n and λ of the model; therefore, in what follows we will consider that λ is an n -dependent variable determined as

$$\lambda = (l/R_0) n - 1. \quad (2)$$

The expression obtained in [3] for free energy on condition that $L = \text{const}$ will be rewritten in a form convenient for subsequent variation:

$$F(n, \lambda) = Lf/R, \quad (3)$$

where

$$f \cong \theta [n \ln n + (1-n) \ln(1-n) + n^2 (1-n)^2 z^2] + \theta \left[\frac{n^2}{2} (1 + (1-n)^2 z) \left(\ln 2 + 2\varphi_1 + \frac{\alpha_1^2}{2\beta_1} \right) \right]. \quad (4)$$

The quantities φ_1 , α_1 , and β_1 involved in (4) are the coefficients of expansion, in a Taylor series, of the average-force potentials [4, 5] which describe the averaged interaction of a singled-out particle (molecule) with particles statistically distributed in the vicinity of the neighboring site of the chain (with allowance for the subsystem of vacancies). These coefficients and the function z are related, by a nonlinear equation, to the coefficients Φ_0 , a , and b of an analogous expansion of the Lennard-Jones potential in small deviations of x of particles from their sites [3, 7].

Having varied (3) by the concentration n with account for the coupling equation (2), we obtain

$$\frac{\partial (f/R)}{\partial n} + \frac{\partial (f/R)}{\partial \lambda} \frac{d\lambda}{dn} = 0 \quad \text{or} \quad \frac{1}{R} \frac{\partial f}{\partial n} - \frac{f}{R^2} \frac{\partial R}{\partial n} + \left(\frac{1}{R} \frac{\partial f}{\partial \lambda} - \frac{f}{R^2} \frac{\partial R}{\partial \lambda} \right) \frac{d\lambda}{dn}, \quad (5)$$

where $\partial R/\partial n = l$, $\partial R/\partial \lambda = R_0$, and $d\lambda/dn = l/R_0 = (1 + \lambda)/n$.

Next, we take into account the fact that the concentration of vacancies $c = 1 - n$ is very low in the crystalline state (of the order of 10^{-5} – 10^{-3}) and use the first approximation ($\alpha_1 = \alpha_0 \cong a$) of the iteration method [3]. As a result, the system of equations from [3, 7] is simplified and transformed to a closed system of four equations for φ_1 , β_1 , β_0 , and z :

$$\ln(\beta_1/2\pi) - a^2/\beta_1 = 0, \quad (6)$$

$$\varphi_1 = \Phi_0 + \frac{a^2}{4\beta_0} - \ln \left(n \sqrt{\frac{\beta_0}{(b + \beta_0)}} \right), \quad (7)$$

$$\beta_1 = b - b^2/(b + \beta_0) \quad \text{or} \quad \beta_0 = \frac{\beta_1 b}{b - \beta_1}, \quad (8)$$

$$z = \sqrt{\frac{1}{2}} \exp \left\{ -\varphi_1 + \frac{a^2}{4\beta_1} \right\} - 1. \quad (9)$$

After computation of the derivatives $\partial f/\partial n$ and $\partial f/\partial \lambda$ with account for expression (4) and system (6)–(9) and their substitution into (5), we write the variational equation in explicit form:

$$\begin{aligned}
\mathcal{F}(n, \lambda(n)) &\equiv \frac{\theta}{R} \left[-\frac{1}{n} \ln(1-n) + n(1-4n+3n^2)z^2 + \frac{n}{2}(1+(1-n)^2z) \left(\ln 2 + 2\varphi_1 + \frac{a^2}{2\beta_1} \right) + \right. \\
&\quad \left. + 2n^2(1-n)^2z \frac{\partial z}{\partial n} + \frac{n^2}{2} \left((1-n)^2 \frac{\partial z}{\partial n} - 2(1-n)z \right) \left(\ln 2 + 2\varphi_1 + \frac{a^2}{2\beta_1} \right) + \right. \\
&\quad \left. + n^2(1+(1-n)^2z) \frac{\partial \varphi_1}{\partial n} \right] + \frac{\theta}{R_0 n} \left[n^2(1-n)^2 \frac{\partial z}{\partial \lambda} \left(2z + \frac{1}{2} \left(\ln 2 + 2\varphi_1 + \frac{a^2}{2\beta_1} \right) \right) + \right. \\
&\quad \left. + \frac{n^2}{2} (1+(1-n)^2z) \left(2 \frac{\partial \varphi_1}{\partial \lambda} + \frac{a}{\beta_1 + a^2} \frac{\partial a}{\partial \lambda} \right) \right] = 0,
\end{aligned} \tag{10}$$

where

$$\frac{\partial z}{\partial n} = \frac{1}{n\sqrt{2}} \exp \left\{ - \left(\varphi_1 + \frac{a^2}{4\beta_1} \right) \right\}; \quad \frac{\partial \varphi_1}{\partial n} = -\frac{1}{n}; \tag{11}$$

$$\frac{\partial \varphi_1}{\partial \lambda} = \frac{\partial \Phi_0}{\partial \lambda} + \frac{\partial \varphi_1}{\partial a} \frac{\partial a}{\partial \lambda} + \frac{\partial \varphi_1}{\partial b} \frac{\partial b}{\partial \lambda} + \frac{\partial \varphi_1}{\partial \beta_0} \frac{\partial \beta_0}{\partial \lambda}; \tag{12}$$

$$\frac{\partial z}{\partial \lambda} = \frac{\partial z}{\partial \varphi_1} \frac{\partial \varphi_1}{\partial \lambda} + \frac{\partial z}{\partial a} \frac{\partial a}{\partial \lambda} + \frac{\partial z}{\partial \beta_1} \frac{\partial \beta_1}{\partial \lambda}; \tag{13}$$

$$\frac{\partial \varphi_1}{\partial a} = \frac{a}{2\beta_0}; \quad \frac{\partial \varphi_1}{\partial b} = \frac{1}{2(b+\beta_0)}; \quad \frac{\partial \varphi_1}{\partial \beta_0} = -\frac{b}{2\beta_0(b+\beta_0)} - \left(\frac{a}{2\beta_0} \right)^2; \tag{14}$$

$$\frac{\partial \Phi_0}{\partial \lambda} = \frac{24}{\theta} \left(-\frac{2}{R_0^{12}(1+\lambda)^{13}} + \frac{1}{R_0^6(1+\lambda)^7} \right); \tag{15}$$

$$\frac{\partial a}{\partial \lambda} = -\frac{144}{\theta} \left(-\frac{4}{R_0^{13}(1+\lambda)^{13}} + \frac{1}{R_0^7(1+\lambda)^7} \right); \tag{16}$$

$$\frac{\partial b}{\partial \lambda} = \frac{72}{\theta} \left(-\frac{52}{R_0^{14}(1+\lambda)^{13}} + \frac{7}{R_0^8(1+\lambda)^7} \right); \tag{17}$$

$$\frac{\partial \beta_0}{\partial \lambda} = \frac{2a\beta_1(b+\beta_0)^2}{(\beta_1+a^2)b^2} \frac{\partial a}{\partial \lambda} - \left(\frac{\beta_0}{b} \right)^2 \frac{\partial b}{\partial \lambda}; \tag{18}$$

$$\frac{\partial z}{\partial \varphi_1} = -(z+1); \quad \frac{\partial z}{\partial a} = -\frac{a}{2\beta_1}(z+1); \quad \frac{\partial z}{\partial \beta_1} = \left(\frac{a}{2\beta_1} \right)^2 (z+1); \tag{19}$$

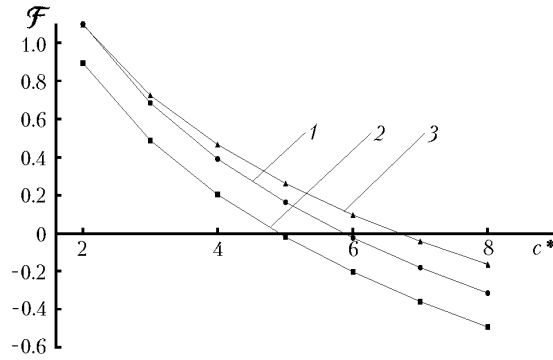


Fig. 1. Dependences of the function $\mathcal{F}(n, \lambda)$ on the concentration of vacancies $c = \mu c^*$ (μ is the scale factor), obtained with account for the coupling equation (2) for fixed parameters $R_0 = 1$ and $\theta = 1$; 1) $l = 0.98$ and $\mu = 10^{-10}$; 2) 1.0 and 10^{-8} ; 3) 1.1 and 10^{-5} .

$$\frac{\partial \beta_1}{\partial \lambda} = \left(\frac{2a\beta_1}{a^2 + \beta_1} \right) \frac{\partial a}{\partial \lambda}. \quad (20)$$

It is noteworthy that, in computation of the derivative $\partial \beta_1 / \partial \lambda$, we have performed implicit differentiation of the transcendental equation (6).

With account for the explicit expressions for the derivatives (11)–(20), the variational equation (10) represents a fairly complex nonlinear equation for whose numerical solution we have employed the Mathematica 3.0 software product. As a result of its solution, we have completed the planned complex program on statistical modeling of the process of uniform deformation of a molecular chain (one-dimensional model of uniaxial extension and compression) with allowance for the interaction between the nearest neighbors in the chain and the correlated distribution of particles and vacancies at the chain sites with simultaneous calculation, in the Gauss approximation, of single- and two-particle distribution functions of particles in the vicinity of the chain sites.

Procedure of Numerical Calculation of the Parameters of the Model and Construction of the Diagram of Extension and Compression. For the molecular chain of length L containing N molecules distributed at M sites ($M > N$) and for prescribed values of the set of the system's external parameters, which includes the dimensionless temperature θ , the molecular length $l = L/N$ (analog of molecular volume), and the length $R_0 = L_0/M_0$ of an undeformed link of the chain, we have selected the n -concentration interval corresponding to the region of obviously crystalline state $n \in [0.9; 1]$. Using the coupling equation (2), we have determined the interval of permissible values of the microdeformations λ of the molecular chain. Next, for each pair of n and λ values we have calculated three coefficients of expansion of the Lennard-Jones potential (Φ_0 , a , and b) and have graphically solved the transcendental variational equation (10) ($\mathcal{F}(n, \lambda) = 0$) in relation to the sought equilibrium value of the concentration n . Simultaneously we have calculated three coefficients of expansion of the average-force potential (ϕ_1 , α_1 , and β_1), the auxiliary correlator z , and all the derivatives involved in the variational equation. The process of its solution is illustrated by the curves given in Fig. 1 for prescribed values of the temperature θ and the molecular length l . The solution of the nonlinear equation that determines the equilibrium value of the concentration n (and the corresponding microdeformation λ) is the point of intersection of the plot of the function $\mathcal{F}(n, \lambda(n))$ and the axis of the concentration $c = 1 - n$.

From the results of numerical solution of the variational equation, we have obtained the dependences of the equilibrium values of the concentration of vacancies c and the microdeformation λ and the corresponding free energy f/n and thermodynamic Gibbs potential g per particle of a molecular chain on its length l ; these dependences are presented in Fig. 2. It is seen that the microdeformation λ depends on l linearly, in practice (Fig. 2a). However, the growth in the concentration c of vacancies under deformation of the chain is described by a nonlinear function of l (Fig. 2b), which, as is well known, contributes to the appearance of dislocations in the specimens in real deformation

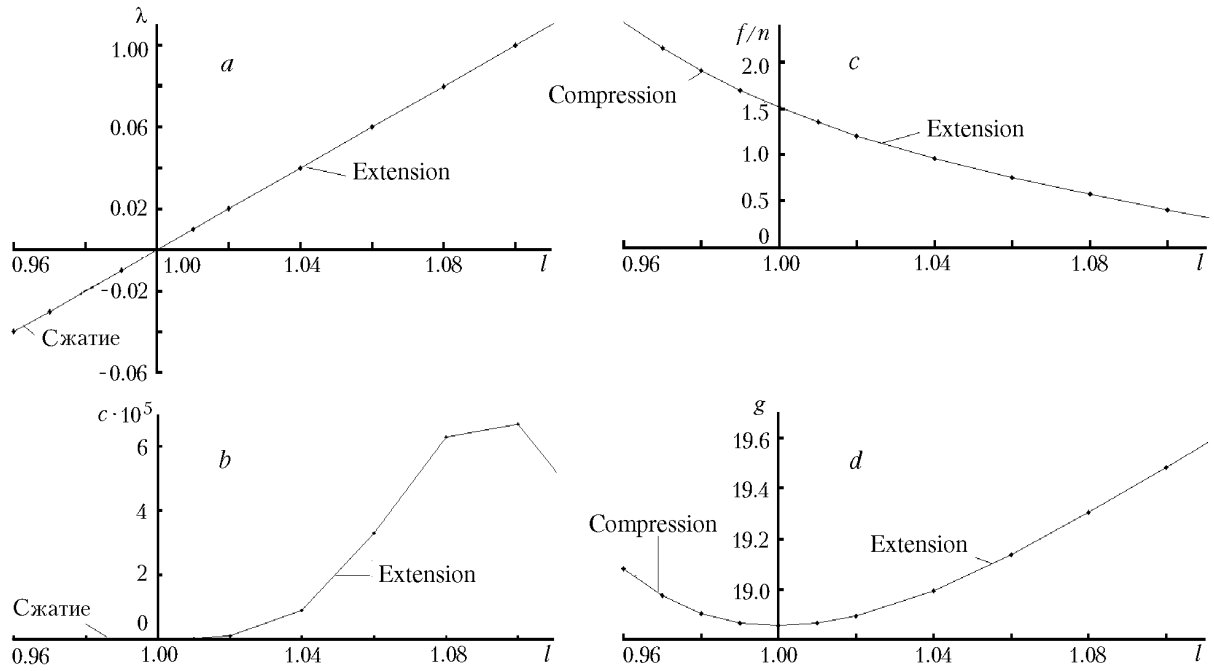


Fig. 2. Microdeformation λ of the chain links (a), concentration of unoccupied sites c (b), and equilibrium free energy f/n (c) and thermodynamic Gibbs potential g (d) per particle vs. molecular length l for fixed parameters $R_0 = 1$ and $\theta = 1$.

processes; these dislocations in turn lead to an increasing influence of plastic deformations. As a result, the process of linear elastic deformation must gradually change to the stage of nonlinear deformation, which will change to the stage of plastic deformations and fluidity of the material with increase in the chain length and vacancy concentration.

Therefore, theoretical construction of the diagram of deformation of a specimen, i.e., searching for the dependence of the stress σ on the value of the relative macrodeformation ε , is a logically successive and final step in creation of the statistical theory of elasticity. Since deformation usually occurs under isobaric-isothermal external conditions in the experiments, for successive description of the structural, thermodynamic, and mechanical properties of macroscopic systems it is convenient to employ the thermodynamic Gibbs potential rather than free energy (Fig. 2c). For the one-dimensional case considered here, the thermodynamic Gibbs potential is determined as follows:

$$G = F(L) + p_0^* L, \quad (21)$$

where p_0^* is a fixed value of the one-dimensional analog of the medium's external pressure, i.e., of the force ensuring the length $L = L_0$ of the chain of N molecules. For convenience of comparison to the three-dimensional case this force is denoted as the pressure (p_0^*), whereas the corresponding deforming force is denoted as the stress (σ^*). Since the free energy is $F = fN/n$ and L is equal to lN , it is more convenient to employ the intensive quantity $g = G/N = f/n + p_0^* l$ (chemical potential) instead of the extensive characteristic represented by the potential G . The analog of normal stress σ^* , i.e., the deforming force, is found from the formula

$$\sigma^* = \frac{1}{L_0} \frac{\partial G}{\partial \varepsilon} = \frac{1}{l_0} \frac{\partial g}{\partial \varepsilon}. \quad (22)$$

The relative macrodeformation ε of the chain will be expressed by the molecular length l :

$$\varepsilon = (L - L_0)/L_0 = (l - l_0)/l_0. \quad (23)$$

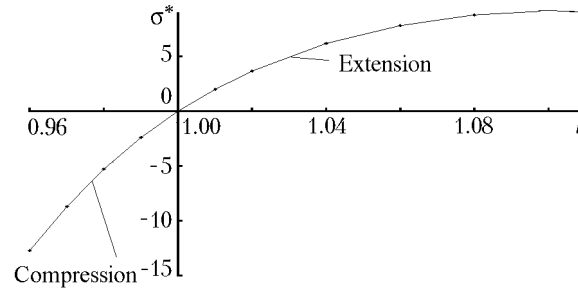


Fig. 3. Diagram of extension and compression of a one-dimensional molecular chain.

As a result, for the deforming force σ^* we obtain

$$\sigma^* = \frac{1}{l_0} \frac{\partial g}{\partial \varepsilon} = \frac{1}{l_0} \frac{\partial g}{\partial l} \frac{\partial l}{\partial \varepsilon} = \frac{\partial g}{\partial l} = \frac{\partial (f/n)}{\partial l} + p_0^* \quad (24)$$

The dependences of the quantity $G = gN$, i.e., the thermodynamic Gibbs potential and the deforming force σ^* (24), on the molecular length l , constructed with the use of the Mathematica 3.0 software product, are presented in Figs. 2a and 3. The left-hand branch of the potential (Fig. 2d) corresponds to the compression of the specimen, whereas the right-hand branch corresponds to its extension. A symmetric, in practice, parabolic portion of this curve in the vicinity of the minimum of the function $g(l)$ determines the region of elastic deformations described by Hooke's law. Next, as the deformation increases, the plot $g(l)$ gradually reaches a virtually linear portion, for which $\sigma^* = \text{const}$ according to (22). The form of σ^* as a function of l is in good agreement with the classical curve of deformation in uniaxial extension and compression of linear specimens. Regions resembling the corresponding portions of elastic and plastic deformations and of fluidity ($\sigma^* = \text{const}$) on the experimental diagrams of stress and deformation are clearly tracked on the right-hand branch corresponding to the extension of the specimen (see Fig. 3).

The results obtained enable us to hope that the statistical theory of elasticity under development will allow a complex description of the structural, thermodynamic, and mechanical properties not only of one-dimensional chains, which is topical at present (in connection with the interest expressed in recent times in molecular chains of different kinds), but also of plane and three-dimensional macroscopic specimens. The properties of such specimens are of importance for traditional problems of elasticity theory.

NOTATION

a and b , coefficients of expansion of the Lennard-Jones potential; c , concentration of vacancies; $\mathcal{F}(n, \lambda)$, notation for the left-hand side of the variational equation; F , free energy of a deformed molecular chain; f , free energy per microcell (or site of the chain); G , thermodynamic Gibbs potential; g , thermodynamic Gibbs potential per particle; k , Boltzmann constant; L and L_0 , length of a deformed and undeformed specimen respectively; l and l_0 , molecular length of a deformed and undeformed link of the chain; T , absolute temperature; M and M_0 , number of microcells into which the entire volume of a deformed and an undeformed system is mentally broken; N , number of particles in the system; n , concentration of molecules in the chain; p_0^* , one-dimensional analog of external pressure in the initial equilibrium undeformed state of a molecular chain; R and R_0 , length of a link of a deformed and undeformed chain; x , coordinate of a particle (molecule) reckoned from the center of the cell (link) of an undeformed chain; z , average value of the Mayer function; α_0 and β_0 and α_1 and β_1 , coefficients of expansion of the average-force potentials $\varphi_0(x)$ and $\varphi_1(x)$; ε , relative macrodeformation of the chain; ε' , depth of the potential well for the Lennard-Jones potential; $\theta = kT/\varepsilon'$, dimensionless temperature; λ , relative deformation of the chain links; σ , normal stress; σ^* , one-dimensional analog of normal stress, i.e., deforming force; Φ_0 , coefficient of expansion (free term) of the pair intermolecular Lennard-Jones potential Φ ; $\varphi(x)$, potential of average forces of interaction of particles; φ_0 and φ_1 , coefficients of expansion of the average-force potentials $\varphi_0(x)$ and $\varphi_1(x)$. Subscripts: *, analog of the corresponding quantity in the three-dimensional case.

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